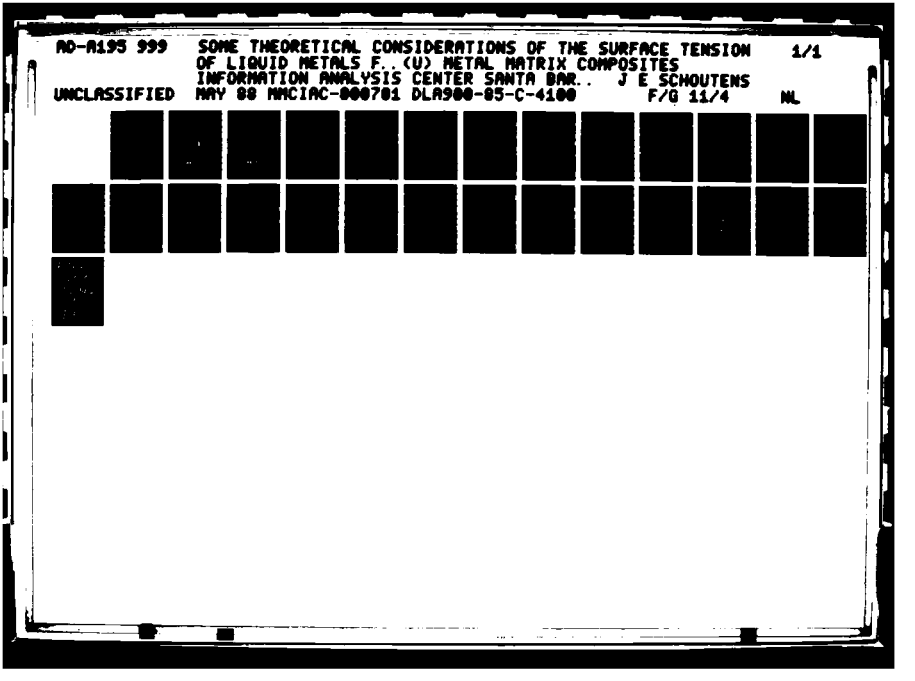
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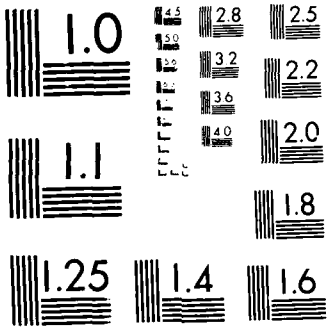

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Manager, Data Analysis
MMCIAC

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This paper presents a model for calculating the surface tension of pure metals and their alloys. It is based upon the theory of Eyring et al. which uses classical statistical physics to describe the thermodynamic properties of metals in the liquid state. Calculations show the surface tension of pure aluminum to be nearly 9 percent greater than that measured for pure aluminum having a monolayer of oxide (Al_2O_3), is within about 10 percent of measured values for Al-xMg and Al-xCu, where x is the weight percent of the alloying element. In the present calculations $0 \leqq x \leqq 8$ wt % for Mg and $0 \leqq x \leqq 30$ wt % for Cu were used. The values calculated are also in good agreement with results from other models. The model was also used to calculate the temperature coefficient. For pure aluminum the calculated values fall within experimental measurements, and exhibit a slight temperature dependence.

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FOREWORD

This Special Technical Paper was prepared under the sponsorship of the Deparment of Defense (DOD) Metal Matrix Composites Information Analysis Center (MMCIAC) operated by Kaman Tempo, Santa Barbara, California. The MMCIAC Special Technical Papers Series includes papers on timely subjects which are judged to be of wide interest to MMCIAC users. Papers in the series comprise results of special research undertaken by the Center staff members, consultants, and subcontractors; invited papers; highly-cited or key journal articles; and research reports for special technical inquiries of MMCIAC users.

This Special Technical Paper is the result of an investigation concerning surface tension of liquid metals undertaken by Jacques E. Schoutens, Manager of Data Analysis and Special Task Services for the MMCIAC.

SOME THEORETICAL CONSIDERATIONS OF THE SURFACE TENSION OF LIQUID METALS FOR METAL MATRIX COMPOSITES

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ABSTRACT

This paper presents a model for calculating the surface tension of pure metals and their alloys. It is based upon the theory of Eyring et al [5] which uses classical statistical physics to describe the thermodynamic properties of metals in the liquid state. Calculations show the surface tension of pure aluminum to be nearly 9 percent greater than that measured for pure aluminum having a monolayer of ~~oxide~~ (Al_2O_3), is within about 10 percent of measured values for Al-xMg and Al-xCu, where x is the weight percent of the alloying element. In the present calculations $0 \leq x \leq 8$ wt % for Mg and $0 \leq x \leq 30$ wt % for Cu were used. The values calculated are also in good agreement with results from other models. The model was also used to calculate the temperature coefficient. For pure aluminum the calculated values fall within experimental measurements, and exhibit a slight temperature dependence.

1. INTRODUCTION

Cast metal matrix composite (MMC) materials reinforced with unidirectional fibers will turn out to be a low cost alternative to MMC fabrication by diffusion bonding, cold and hot compaction, and other methods. In the development of this kind of casting technology, one of the most important problems to be solved is wetting of the fibers. From an experimental point of view, wettability is poorly understood. From the theoretical point of view there are a number of different approaches, and some of the sophisticated approaches have not been of use to experimentalists. There are a number of approaches for calculating the thermodynamic and surface properties of liquid metals, and they divide into macroscopic and microscopic models.

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The macroscopic modeling approach is the most general and is based on equilibrium thermodynamics. It uses the classical Gibbs formulation for an interphase, and attempts to predict interfacial tension or adhesion and the surface free energy of liquid metal in equilibrium with its vapor, or another liquid, or a solid substrate. The Gibbs model is an energy balance between the Helmholtz-free energy and the sum of entropy, mechanical work, surface tension and the chemical potential of the species involved. From this balance the surface free energy is related to the wettability of the liquid metal on a non-metallic substrate material, and wettability is then related to the contact angle using Young's equation. It is well known experimentally that the wetting of a ceramic by a liquid metal can be inferred from changes in the contact angle with changes in the parameters of the experiments. Consequently, this king of modeling is used to "estimate" the wettability of ceramics by liquid metals under specific conditions. What is most often the case is the Gibbs formulation is used post facto to explain what happened in an experiment, and, therefore, does not really possess much of a what a good theory should possess: predicting the outcome of an experiment!

Various kinds of micro-models have been proposed which attempt to introduce an atomic or molecular "picture" into thermodynamic arguments. Included in this type of approach is the notion that the major contribution to adhesion forces arises from the instantaneous attraction among dipoles and among induced dipole interactions between the liquid and it substrate. This method has been fairly successfully applied to understand hydrocarbons wetting solid hydrocarbons and similar conditions in organic chemistry. These interactions are modeled variously with the well-known Lennard-Jones, Devonshire or Morse potentials, and with the London formula which involves first ionization potentials of constituents. Another approach of the micro-model type argues that the basic parameter behind the empirical relationship between surface tension and heat of vaporization per unit atomic surface is the electron density at the boundary of the Wigner-Seitz atomic cell. It was shown by Miedema and co-workers [1-3] that the surface energy and the heat of vaporization are linearly related to the Wigner-Seitz cell by empirical scaling rules. These models then embody a combination of behaviors at the microscopic and at the macroscopic levels.

Finally, there are theories of liquid metals that are derived ab initio. These formal approaches are rigorous mathematically and generally elegant. Approximations are introduced at the end, either in the form of simplified mathematics or over-simplified radial distribution functions and inter-molecular potentials. These theories are not really suitable for practical approaches to predict wettability or interfacial energies or for guiding experiments; they are tools to understand fundamental properties of liquid metals. The interested reader is referred to a review of the literature [4].

The approach taken in the work reported herein is intermediate between thermodynamic macro-models and detailed theoretical models.

1. THEORY

The theory discussed here is based on classical statistical mechanics first developed by Eyring and co-workers [5,6] to predict thermodynamic properties of liquids. Eyring's theory is founded on the assumption that the metal upon melting acquires vacancies that are moving freely through the melt and that there is short-range order in the liquid but no long-range order. These freely moving vacancies, called fluidized vacancies, have a volume fraction that is made to cor spond to the volume change of the metal upon melting, or about 3 to 4 percent for transition and non-transition metals. Using statistical mechanics partition functions are written which account for the gas-like behavior of the fluidized vacancies, and for the solid-like behavior of the liquid metal. The relationship between the Helmholtz free energy and the partition functions make it possible to calculate the thermodynamic properties of the liquid metal. Eyring and co-workers have shown this approach to be quite successful in predicting the thermodynamic properties of a large number of liquids, including a number of pure metals. However, calculations of the surface tension of liquid metal alloys using this approach has not been reported. The work reported herein is a first attempt at calculating the surface tension of pure aluminum and binary alloys of aluminum such as Al-Cu and Al-Mg.

The relationship between the Helmholtz free energy and the partition function for a liquid is

$$A = - kT \ln f \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature, and f is the partition function. The surface tension is calculated from

$$\gamma = \left(\frac{\partial A}{\partial \Omega}\right)_{N,v,T} \tag{2}$$

where N is Avogadro's number, V is the molar volume and Ω is the surface area occupied by a monolayer of atoms on the liquid surface, which is given by

$$\Omega = \omega N_c \tag{3}$$

where ω is the area occupied by one atom, and N_c is the total number of sides available for atoms on the liquid surface. To calculate the Helmholtz free energy, the partition function can be written as the product

$$f' = f_B f_{mL} \tag{4}$$

where f_{ml} is the partition function for the surface atoms and f_B is the partition function for the bulk liquid atoms. In general, any partition function can be written as the product of partition functions describing each process involved [7]. Therefore [5]

$$f_B^{N_B} = (f_s)^{N_B V_s/V} (f_g)^{N_B(1-V_s/V)} \tag{5}$$

where V_s is the molar volume of the metal at its melting point, and

$$V = \frac{M}{\rho(T)} \tag{6}$$

is the molar volume of the liquid at temperature T when its density $\rho(T)$ is a function of temperature, and M is the atomic weight of the metal under

consideration. In Equation 5, f_s is the partition function for the solid-like behavior of the bulk liquid and f_g is the partition function for the gas-like behavior. The partition function can be further separated into the product of partition functions, thus

$$f_s = f_{Einstein}\, f_{rot}\, f_{vib}\, J(T) \tag{7}$$

and

$$f_g = f_{trans}\, f_{rot}\, f_{vib} \tag{8}$$

showing that rotation, vibration, and translation motion can be accounted for in this manner. J(T) is the partition function for internal degrees of freedom. The partition function for the oscillations of the atoms in the solid may be calculated from Einstein's theory, or

$$f_{Einstein} = \frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3} \tag{9}$$

where θ is the Einstein temperature [8]. For metals, $\theta/T \ll 1$ so that Equation 9 reduces to

$$f_{Einstein} \cong \exp(E_s/RT) \tag{10}$$

where E_s is the sublimation energy and R is the universal gas constant.

For pure liquid metals, the probability of diatomic modules is extremely small, and those formed with residual impurities in the metal is also very small. Consequently, the partition functions for rotation and vibration are unity.

A term must be included in the partition function given by Equation 7 to account for the total number of positions available to an atoms in the melt, or [5]

$$1 + n\left(\frac{V-V_s}{V_s}\right) \exp\left\{-\frac{aE_s V_s}{(V-V_s)RT}\right\} \tag{11}$$

where n and a are parameters that can be calculated theoretically. It will be seen shortly that in the further development of the theory, these two parameters drop out.

The partition function for the bulk behavior of the liquid is then written as

$$f_B^{N_B} = \left\{ \frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3} \left[1 + n \left(\frac{V-V_s}{V_s} \right) \exp \left\{ - \frac{aE_s V_s}{(V-V_s)RT} \right\} \right] \right\}^{N_B V_s/V} * \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} (V-V_s) J(T) \right\}^{N_B(1-V_s/V)} \left\{ \left[\frac{N_B(V-V_s)}{V} \right]! \right\}^{-1} \quad (12)$$

A similar reasoning gives the partition function for the monolayer or

$$f_{mL}^{N'} = \left\{ \frac{e^{E'_s/RT}}{(1-e^{-\theta'/T})^3} \left[1 + n' \left(\frac{V-V_s}{V_s} \right) \exp \left\{ - \frac{a'E'V_s}{(V-V_s)RT} \right\} \right] \right\}^{N'V_s/V} * \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} (V-V_s) J'(T) \right\}^{N'(1-V_s/V)} \left\{ \left[\frac{N'(V-V_s)}{V} \right]! \right\}^{-1} \quad (13)$$

The second brackets in Equation 12 and 13 can be simplified using Stirlings approximation $x! = (x/e)^x$ so that

$$f_g^{N_B(1-V_s/V)} = \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\frac{eV}{N} \right) \right\}^{N_B(1-V_s/V)} \quad (14)$$

and

$$f_g^{N'(1-V_s/V)} = \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\frac{eV}{N} \right) \right\}^{N'(1-V_s/V)} \quad (15)$$

In Equation 13, the primed quantities refer to the surface atoms corresponding to the un-primed quantities. In the above derivation we must have conservation of the number of atoms, or

$$N = N_B + N' \quad (16)$$

where N_B is the number of atoms in the bulk and N' the number of atoms on the surface as a monolayer.

Now we write

$$\ln f' = \ln(f_B f_{mL}) = \ln_B + \ln_{fmL} \tag{17}$$

and using Equations 12 through 15 gives

$$\ln f' = N' \frac{V_s}{V} \left\{ \ln \frac{f_s' \left[1 + n' \left[(V/V_s)-1\right] \exp[-a'E_s'V_s/(V-V_s)RT]\right)}{f_s \quad 1 + n \quad \left[(V/V_s)-1\right] \exp[-aE_sV_s/(V-V_s)RT]} \right\} + \ln f, \tag{18}$$

where

$$f_s = \frac{\exp[E_s/RT]}{(1-e^{-\theta/T})^3} \quad , \qquad f_s' = \frac{\exp[E_s'/RT]}{(1-e^{-\theta'/T})^3} \quad .$$

The Helmholtz free energy for a liquid involving its surface is

$$A = - kT \ln f' \tag{19}$$

and

$$\gamma = \left(\frac{\partial A}{\partial \Omega}\right)_{N,V,T} = \omega^{-1} \left(\frac{\partial A}{\partial N_c}\right)_{N,V,T} = \omega^{-1} \left(\frac{V_s}{V}\right) \left(\frac{\partial A}{\partial N'}\right)_{N,V,T} \tag{20}$$

In Equation 20, a random distribution of vacancies is assumed, that N_c is the total number of sites available for atoms on the surface, and

$$\frac{N'}{N_c} = \frac{V_s}{V} \quad . \tag{21}$$

Combining Equation 18, 19 and 20 gives after some algebra [9]

$$\gamma = \omega^{-1} \left(\frac{V_s}{V}\right)^2 kT \left\{ \ln \left(\frac{f_s}{f_s'}\right) + \ln g_r \right\} \tag{22}$$

where

$$\ln g_r = \frac{1 + n \quad \left[(V/V_s)-1\right] \exp[-aE_sV_s/(V-V_s)RT]}{1 + n' \left[(V/V_s)-1\right] \exp[-a'E_s'V_s/(V-V_s)RT]} \quad , \tag{23}$$

Because $n' \cong n$ and $a' \cong a$, $g_r \cong 1$ and hence $\ln g_r = 0$ and Equation 22 reduces to

$$\gamma = \omega^{-1} \left(\frac{V_s}{V}\right)^2 kT \left[\frac{E_s - E_s'}{RT} + 3 \ln \frac{(1-e^{-\theta'/T})}{(1-e^{-\theta/T})} + \ln \frac{J(T)}{J'(T)}\right] \quad (24)$$

It can be shown that $\ln[J(T)/J'(T)] = 0$. Lu, Jhon, Ree and Eyring showed that

$$E_s' \cong \frac{3}{4} E_s (1 + f) \quad (25)$$

and

$$\theta' = \theta \left(\frac{3}{4} + \frac{3}{4} f\right)^{\frac{1}{2}} \quad (26)$$

so that the second term in the bracket of Equation 24 reduces

$$\frac{3}{2} \ln \frac{3}{4}(1 + f) \quad .$$

Then, we finally have that

$$\gamma = \omega^{-1} \left(\frac{V_s}{V}\right)^2 kT \left[\frac{E_s}{4RT} (1-3f) + \frac{3}{2} \ln \frac{3}{4}(1+f)\right] \quad . \quad (27)$$

In Equation 27, for close packing

$$\omega = \frac{\sqrt{3}}{2} \left(\frac{\sqrt{2}\, V_s}{N}\right)^{2/3} \quad . \quad (28)$$

3. NUMERICAL RESULTS AND DISCUSSION

We will now perform three calculations: one for pure aluminum, one for Al-Cu alloy and Al-Mg.

3.1 Pure Aluminum

Table I present the numerical values of the parameters used in the calculation of surface tension of pure aluminum. To calculate the surface tension of pure liquid aluminum the temperature dependent density values of Gebhardt et al. [11] were used. Between 933° and 1173°K, these values are well represented by

$$\rho(T) = 2.368 - 2.63 \times 10^{-4}(T-T_m) \qquad (29)$$

where T_m = 933°K is the melting temperature of pure aluminum and T is the temperature of interest in °K. The values calculated with Equation 29 differs by 0.71 percent at the melting point from values obtained with a similar expression reported elsewhere [12], and 0.56 percent at 1173°K, the values obtained with Equation 29 being lower than those obtained with a similar equation [12] by the indicated percentages. The molar volume, V_s, for pure aluminum given in Table I differs from that given by Shimoji [4] which is 11.4 cm^3/g-atom.

Figure 1 shows the surface tension of pure aluminum as a function of temperature calculated with Equation 27. These values are compared with other calculated values [9,13.15] and measured values [9,14,16]. Also shown is a range of values at 660°C of the surface tension of pure aluminum measured by Garcia-Cordovilla and co-workers [13] using the method of maximum bubble pressure. They found that the surface tension of pure aluminum was a high as 1122 mJm^{-2} [16] for an unoxidized bubble surface, decreasing to 865 mJm^{-2} with a controlled increase in the bubble surface oxidation. The values calculated with Equation 27, are in good agreement with other computations using various modeling approaches, and measured values reported in the literature.

There is an interesting implication from the range of measured surface tension values shown in Figure 1 and reported by Garcia-Cordovilla et al. [16]. These suggest that the values reported by others [9,14,17-26] are low because the surface was contaminated by oxides during surface tension measurements. Indeed, measurements of surface tension of aluminum requires great care that no oxygen is introduced into the system except under controlled conditions.

The surface tension value of 1184 mJm^{-2} shown in Figure 1 was calculated by Chacon et al [13] for a free surface of pure aluminum. This value is thus still greater, by 5.2 percent, than the highest measured value [16,26] under conditions of ultra-high vacuum, or with a clean and purges system and using argon gas having a purity of 99.9995 percent. Moreover, to attain such measured high surface tension values, high purity (99.999 percent) aluminum was used [26]. The drop in the surface tension from 1122 mJm^{-2} to a mean value of 868 mJm^{-2} [16,26] has been established as caused by a monolayer of oxide, presumably Al_2O_3 [26].

3.2 Aluminum-Magnesium Alloy

For the case of binary alloys, Equation 27 was modified by using rule-of-mixture types of scaling. If the alloy is designated as Al-xMg, where x is the weight percent, then the following rules of mixtures can be used. The area occupied by the atom, ω, can now be assumed to have the value

$$\omega = (1-x_1)\omega_{Al} + x_1\omega_{Mg} \tag{30}$$

where x_1 is the fraction by volume. The molar volume of the alloy can be written similarly as

$$V_s = (1-x_1)V_{sAl} + x_1V_{sMg} \tag{31}$$

and the molar volume of the alloy as a function of temperature can be written

$$V = (1-x_1)\frac{M_{Al}}{\rho_{Al}(T)} + x_1\frac{M_{Mg}}{\rho_{Mg}(T)}$$

$$\cong \left[(1-x_1)M_{Al} + x_1M_{Mg}\right]\frac{1}{\rho(T)} \tag{32}$$

where X_1 is on the order of a few percent in this calculation. For the density relation we used the following

$$\rho(T) = 2.376 - 2.8 \times 10^{-4}(T-T_m) - 0.9x_1 \tag{33}$$

where the last term is to account for the observation that the density of the alloy varies linearly with magnesium content [16]. The following equation was used to calculate the dissociation energy for the alloy [27],

$$E_s = (1-x_l)^2 E_{sAl} + x_l^2 E_{sMg} + 2x_l(1-x_l)\sqrt{E_{sAl}E_{sMg}} \quad . \qquad (34)$$

These modifications were made to Equation 27, and the following values were used in addition to those shown in Table I: E_{sMg} = 32.9498 kcal/mole, V_{sMg} = 14.821 cm^3/g-atom, M_{Mg} = 24.32 gm/mole.

Figure 2 shows calculated values of surface tension for Al-xMg, where $0 \leq x \leq 8$ wt % Mg. These results are compared with measured values reported by Garcia-Cordovilla and co-workers for the unoxidized and the oxidized state. The same data were replotted as a function of magnesium content at 973°K, and are shown in Figure 3. The results of the present calculation fall between the results for unoxidized and oxidized measured values [16], the entire range being about 22 percent.

3.3 Aluminum-Copper Alloy

The calculation described for Al-xMg alloy were repeated for Al-xCu alloy, with $0 \leq x \leq 30$ wt % copper. The results of these calculations are plotted in Figure 4. These results are compared with measurements reported by Eremenko et al [28] and Laty et al [29]. It should be noted that the present results are about 6 percent higher than the values measured at 973°K for 20 wt% copper. Unlike the results for Al-xMg, the surface tension of this alloy increases with increasing weight percentage of copper. This is shown in Figure 5 where the results of the present calculations are compared with the results of calculations performed by Poirier and Speiser [15]. In this calculation the liquidus temperatures of Al-Cu binary corresponding to the wt% of copper were used. These results give a curve which is parallel to the curve calculated by Poiriet and Speiser [15], who used a thermodynamic model to obtain their results. The present results give surface tension values for Al-xCu that is higher than Poirier and Speiser's result by approximately 8 percent.

3.4 Temperature Coefficient.

The temperature coefficient can be calculated directly from Equation 27 by differiention with respect to T. This gives the following result

$$\frac{d\gamma}{dT} = \frac{3k}{\omega}\left[\frac{V_s}{V(T)}\right]^2 \ln\frac{3}{4}(1+f) - 5.26 \times 10^{-4}\ \frac{\gamma(T)}{\rho(T)} \qquad (35)$$

where the temperature dependence of the molar volume and density is shown to emphasize the fact that $d\gamma/dT$ has a temperature dependence. It is easily shown that the first term of Equation 35 is approximately 25 percent that of the second term. Calculated values of the temperature coefficient as a function of temperature for pure aluminum are shown in Table II. From these results, we note that the temperature coefficient has a weak dependence on temperature, decreasing by 5.8 percent over a temperature range of 300 degrees.

It is worth noting that the calculated value of the temperature coefficient falls well within the experimentally determined range, this range varying from a minimum value of -0.12 [24,26] to a maximum value of -0.51 [18] for pure aluminum, using various experimental methods. This wide range in measured values is attributable to the many difficulties encountered in making measurements of surface tension of liquid metal even though they are based on well-known techniques in classical physics.

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Table 1. Numerical values used for calculating the surface tension of pure aluminum with equation 27.

Parameter	Numerical Value	Ref.
f	0.083	9
V_s, cm^3/g-atom	10.6327	9
E_s, kcal/mole	64.5098	9
M, gm/mole	26.982	10
k, erg/°K	1.3807×10^{-16}	
R, erg/°K mole	8.314×10^{7}	
N, atoms/mole	6.023×10^{23}	

Table II. Calculated values of the temperature coefficient for pure aluminum.

T(°K)	$\gamma(T)$*	V(T)	$\rho(T)^+$	$d\gamma/dT$
973	938	11.448	2.357	-0.260
1073	911	11.574	2.331	-0.255
1173	884	11.706	2.305	-0.250
1273	858	11.842	2.279	-0.245

*calculated with equation 27
+calculated with equation 29

LIST OF FIGURES

fig 1

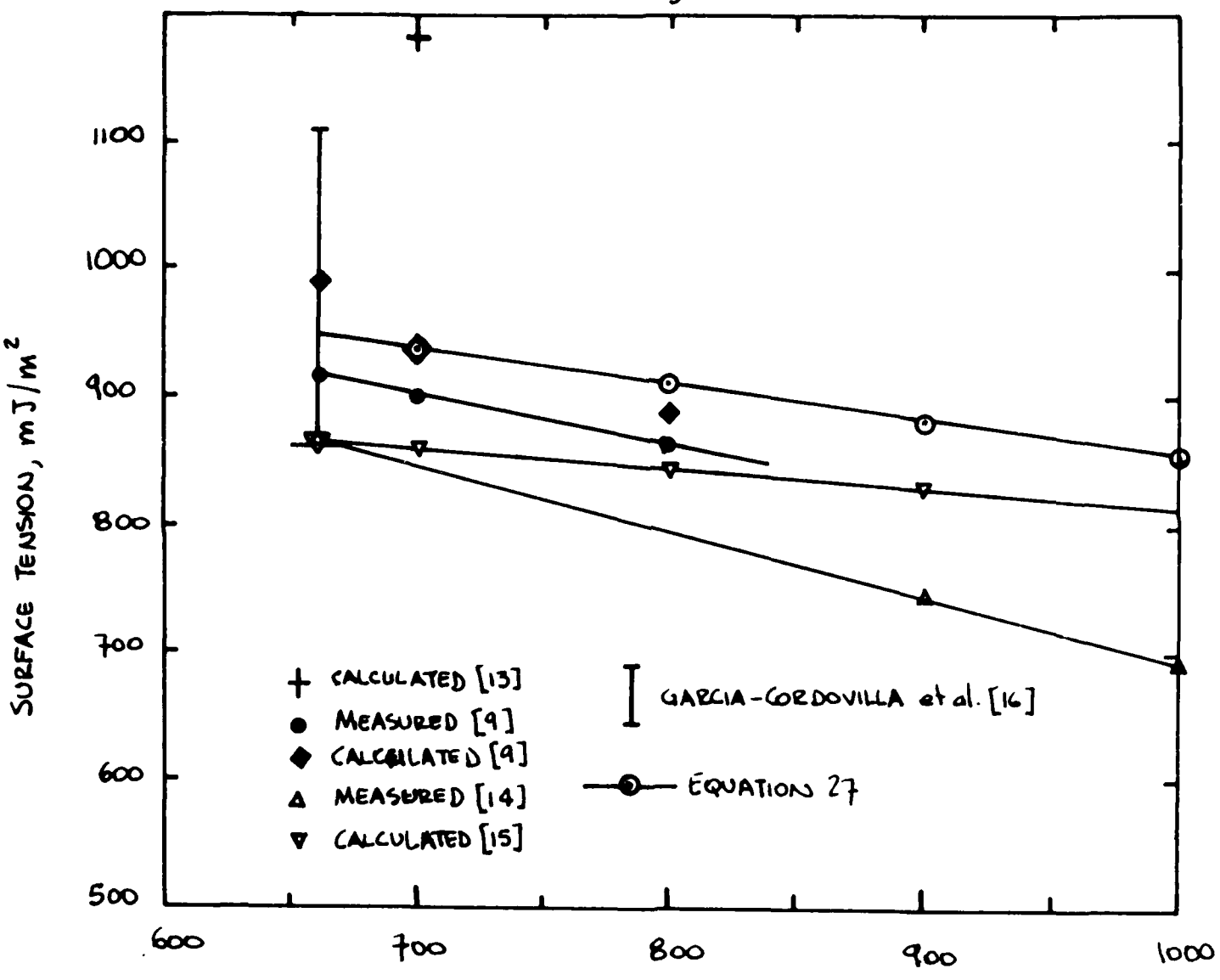

1100
1000
900
800
700
600
500
SURFACE TENSION, mJ/m²
600
700
800
900
1000
TEMPERATURE, °C
CALCULATED [13]
MEASURED [9]
CALCULATED [9]
MEASURED [14]
CALCULATED [15]
GARCIA-CORDOVILLA et al. [16]
EQUATION 27

fig 2

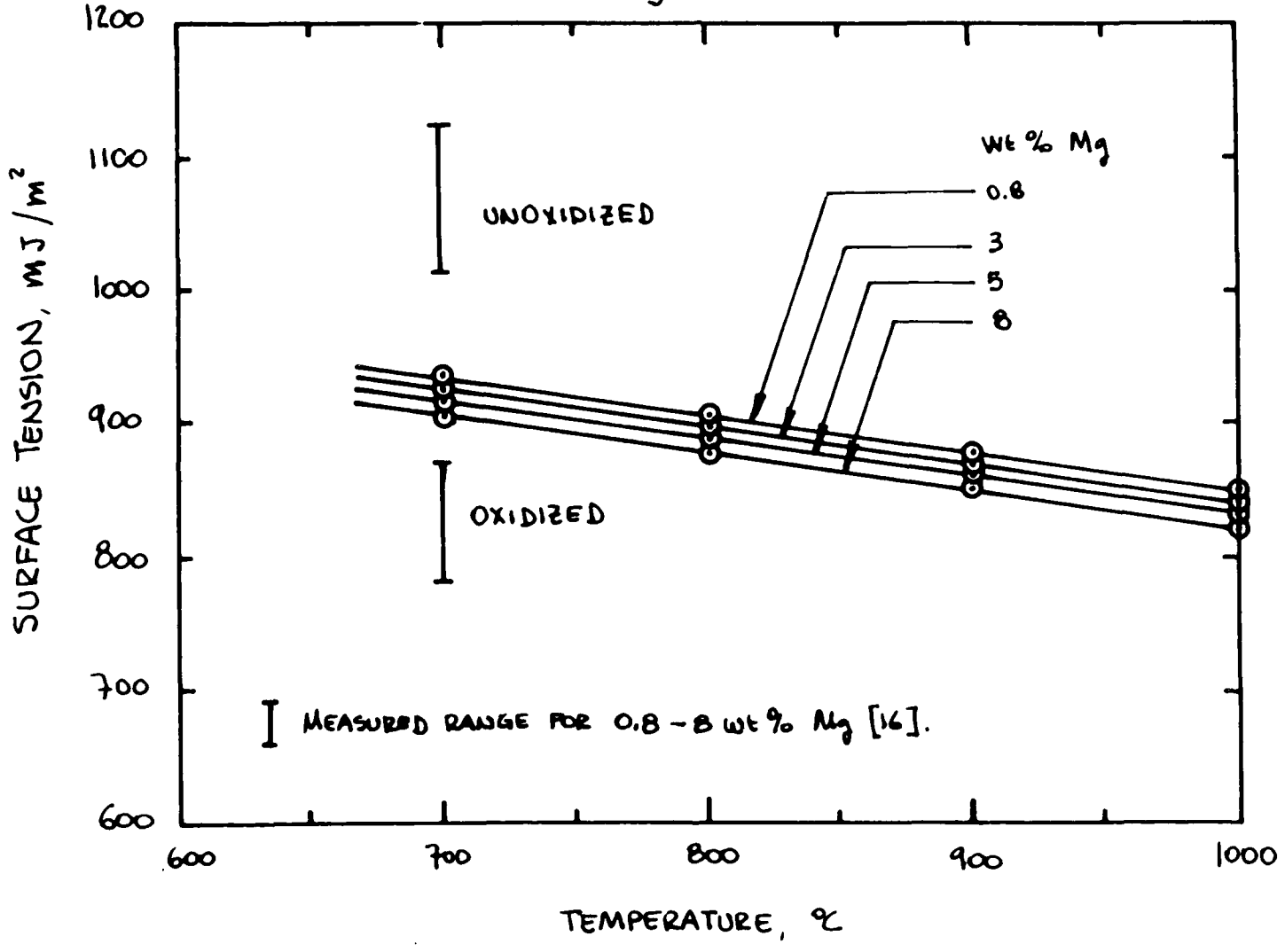

1200
1100
1000
900
800
700
600
SURFACE TENSION, mJ/m²
UNOXIDIZED
OXIDIZED
Wt % Mg
0.8
3
5
8
MEASURED RANGE FOR 0.8 - 8 wt % Mg [16].
600
700
800
900
1000
TEMPERATURE, °C

fig. 3

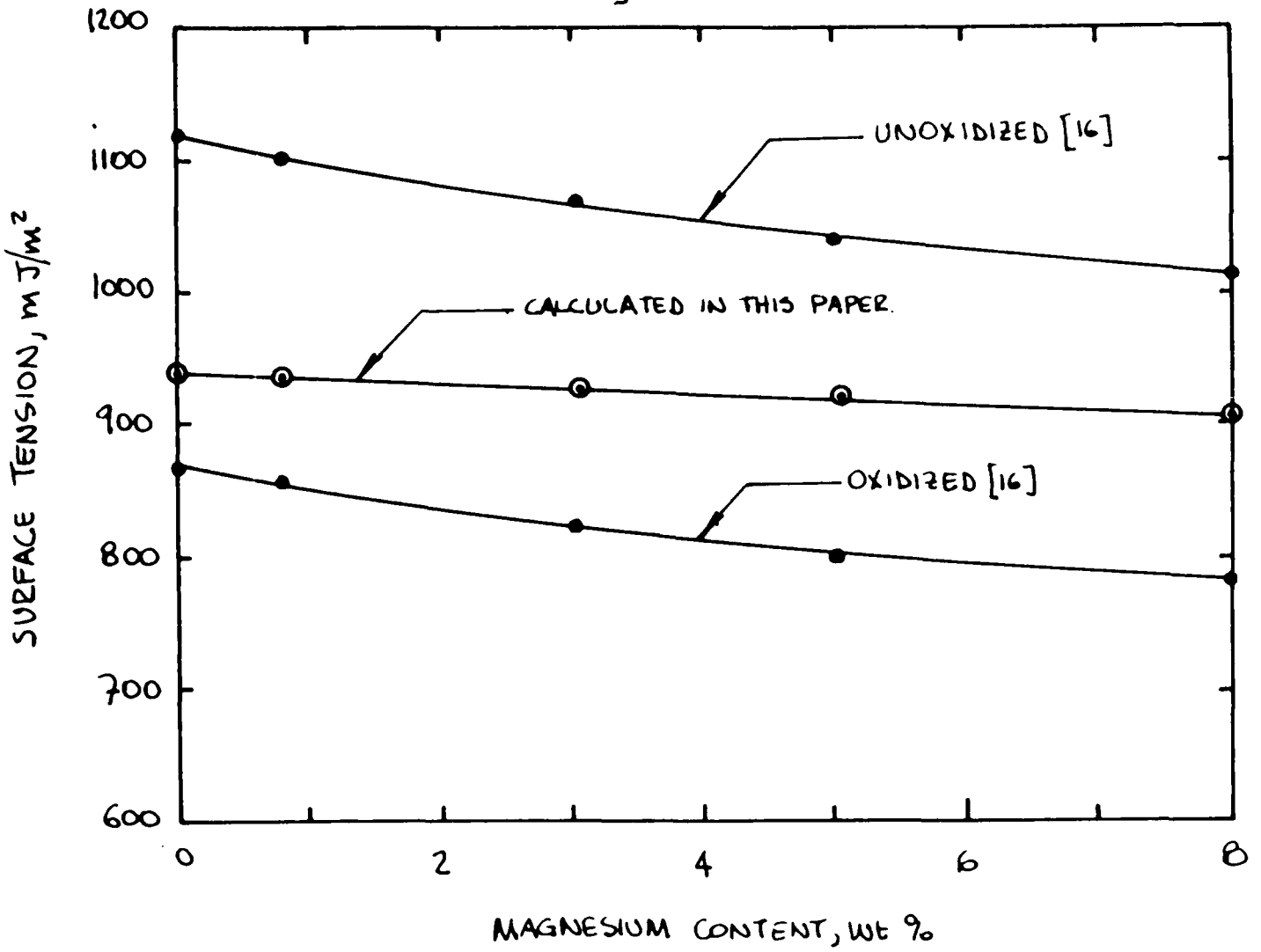
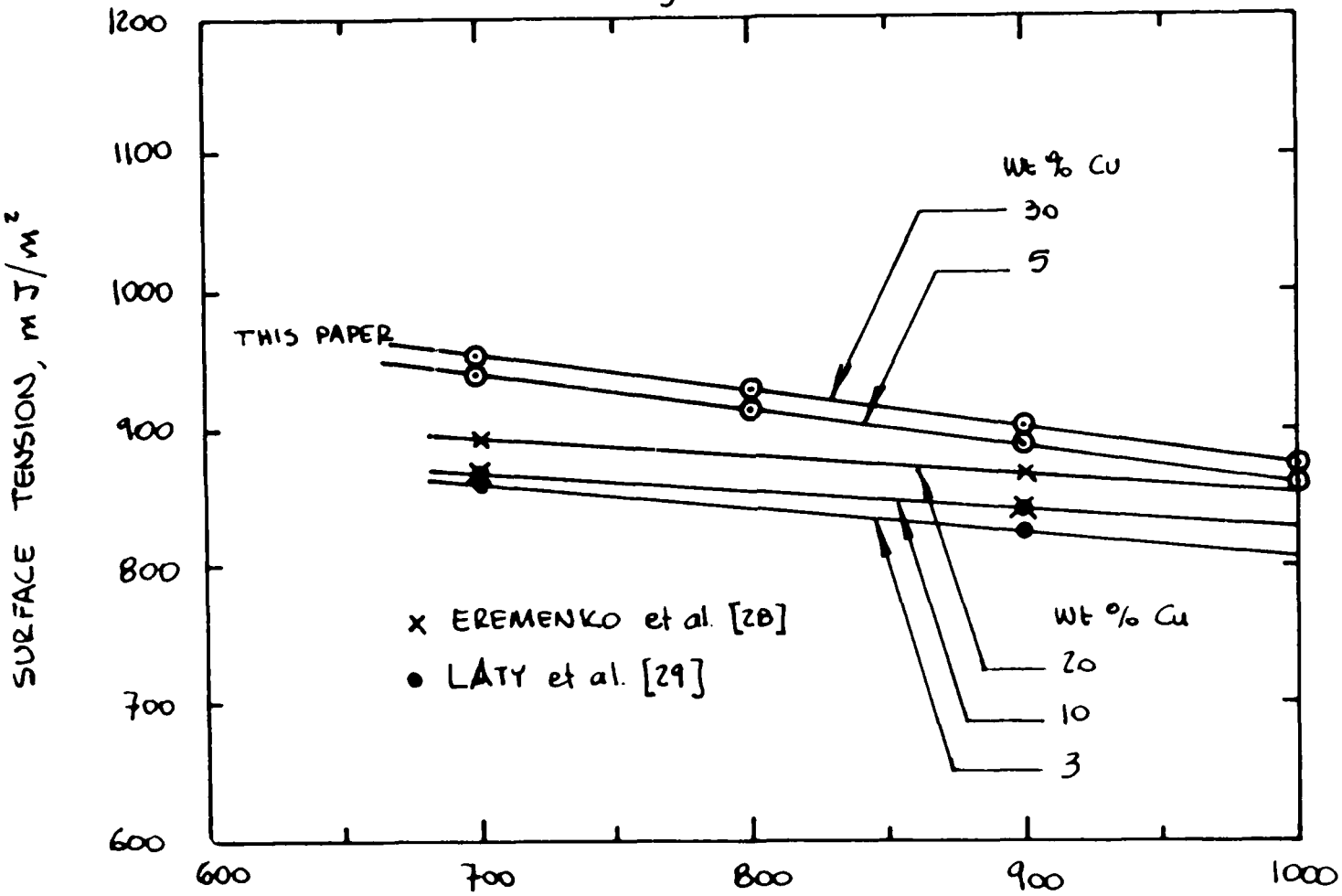

1200
1100
1000
900
800
700
600
SURFACE TENSION, mJ/m²
UNOXIDIZED [16]
CALCULATED IN THIS PAPER.
OXIDIZED [16]
0
2
4
6
8
MAGNESIUM CONTENT, Wt %

fig.4


1200
1100
1000
900
800
700
600
600
700
800
900
1000
SURFACE TENSION, mJ/m²
TEMPERATURE, °C
THIS PAPER
Wt % Cu
30
5
20
10
3
× EREMENKO et al. [28]
● LATY et al. [29]

END

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